PROCESS FOR THE PREPARATION OF STILBENE/STYRENE-COPOLYMERS

Description

The invention pertains to a process for the preparation of copolymers based on 1,2-diphenyl ethene, in particular trans-1,2-diphenyl ethene (trans-stilbene) and styrene.

Stilbene/styrene-copolymers can be used in the art in polystyrene applications which require a high thermal stability.

The polymerisation of trans-stilbene and styrene is known in principle. In *Journal of Polymer Science, Part B, Polymer Letters*, Vol. 2, 1964, pp. 1121 - 1125 the anionic polymerisation of styrene with trans-stilbene is described. The polymerisation in that case was carried out using n-butyl lithium at a temperature of 60°C for 1 - 9 days. In this process, however, only styrene-rich copolymers were obtained. The polymers could be isolated by means of extraction. In the case of copolymerisation in benzene a product was obtained in a yield of 72% which had a softening point of 148°C and a reduced viscosity of only 0.12 dl/g.

In *Bull. Chim. Soc. Jap.* Vol. 41, pp. 1940 - 1944 (1968) the reaction of trans-stilbene and styrene with n-buthyl lithium is described. As solvent THF and benzene were used. The monomers and the initiator were mixed and reacted. The obtained product had a viscosity in benzene of C = 1.0 g/dl at 30°C. The yield in THF was 68%. In the case of reaction in benzene the yield was only 24%.

For technical applications trans-stilbene/styrene-copolymer with a high trans-stilbene content is required, which has a high molecular weight and a high glass temperature. The softening point or the glass temperature should preferably be at least 120°C, especially preferably at least 130°C. The yield should preferably be at

least 70%. The limiting viscosity, measured in toluene at 30°C, should preferably be at least 0.6 dl/g. Preferably, the copolymers should have a molecular weight M_W of at least 100,000 g/mol.

The present invention has for its object to make available a processs for the preparation of copolymers based on 1,2-diphenyl ethene and styrene which leads to technically applicable copolymers which preferably meet the requirements indicated above.

The problem is solved according to the invention by means of a process for the preparation of copolymers based on 1,2-diphenyl ethene and styrene by polymerisation of the monomers

a) 1 - 63 wt.% of 1,2-diphenyl ethene, wherein the aromatic nuclei can be substituted by up to 5 C_{1-12} alkyl groups, as component A,

b) 37 - 99 wt.% of styrene, wherein the aromatic nucleus can be substituted by 5 C_{1-12} alkyl groups, as component B,

c) 0 - 50 wt.% of further copolymerisable monomers as component C,

with the overal amount of components A, B, and C being 100 wt.%, with component A and an initiator being put in and components B and optionally C being continuously dosed to the polymerisation mixture.

It was found that copolymers with the desired properties are obtained when in particular trans-stilbene is put in and styrene is continuously dosed to the polymerisation mixture.

The monomer content of component A preferably is 10 - 63 wt.%, in particular 15 - 30 wt.%. The content of component B preferably is 37 - 90 wt.%, in particular 70 - 85 wt.%. The content of component C preferably is 0 - 30 wt.%, in particular 0 - 10 wt.%.

As component A 1,2-diphenyl ethene is used wherein the aromatic nuclei can be sunstituted by up to 5, preferably up to 2 C_{1-12}, preferably C_{1-6} alkyl groups. Especially preferably there are no substituents. The 1,2-diphenyl ethene derivatives are preferably used in the trans-form. In particular trans-stilbene is used as component A.

As component B styrene is used wherein the aromatische nucleus can be substituted as is described for component A. Especially preferably styrene is used.

As component C optionally further copolymerisable monomers can be used which in particular can be anionically polymerised. Examples of suitable monomers of component C are butadiene, isoprene, α-methyl styrene and methyl(meth)acrylate.

Preferably essentially only stilbene and styrene are present as monomers.

The polymerisation can be carried out with any polymerisation initiators desired. In this process a radical, cationic or anionic polymerisation is possible. Preferably the polymerisation is carried out anionically.

The polymerisation temperature in this process generally is 0 - 130°C, preferably 50 - 90°C. In general, polymerisation takes place under isothermal conditions, i.e. with the polymerisation temperature being kept constant. It is also possible to let the temperature rise in the range of 0 - 130°C, for instance from 30 to 120°C. It is especially effective to first polymerise isothermally and then, near the end of the polymerisation, i.e. at low monomer concentrations, to let the temperature rise adiabatically in order to keep the polymerisation times brief.

The polymerisation can be carried out at a pressure in the range of 1 - 10 bar. As a rule, it is carried out at ambient pressure.

The reaction times as a rule are in the range of 0.1 - 24, preferably 0.5 – 12, and especially preferably 1 - 10 hours.

According to the process according to the invention for the preparation of copolymers component A is put in and components B and optionally C are dosed during the reaction, preferably according to such a gradient process that with increasing duration of the reaction, the amount of monomers of component B added per unit of time is essentially reduced in accordance with the still present amount of monomers of component A. By this type of reaction the monomer ratio is kept almost constant during the entire polymerisation. To control the supply gradient advantageous use can be made of the change of the index of refraction, which is a function of the monomer ratio. A further possibility consists in that in a series of preliminary tests the monomer ratio is determined as a function of the reaction and in this way a corresponding calibration curve is obtained.

The reaction of said monomers preferably takes place in an inert solvent. By "inert" is meant in this case that the solvent does not react with the organometallic initiators commonly used to initiate the reaction. In general hydrocarbons are suitable as solvent. These may be aliphatic, cycloaliphatic as well as aromatic hydrocarbons. Preferably the hydrocarbon is selected from benzene, toluene, ethyl benzene, cyclohexane, methyl cyclohexane, and xylene, as well as mixtures thereof.

Also hydrocarbons may be used where the copolymer formed in the course of the reaction is not soluble. In this case instead of the solution polymerisation a precipitation polymerisation may be carried out or a dispersion polymerisation

using a dispersing aid. As reaction medium for such processs variants are suitable, e.g., butane, pentane, n-hexane, isopentane, heptane, octane, and isooctane. The polymerisation is generally initiated by means of organometallic compounds (anionic polymerisation). Preferably, use is made of compounds of alkali metals, in particular of lithium. Examples of suitable initiators are methyl lithium, ethyl lithium, propyl lithium, n-butyl lithium, sec-butyl lithium, and tert.-butyl lithium. In particular sec-butyl lithium is employed. The organometallic compound as a rule is added as a solution in a chemically inert hydrocarbon. The dosing follows the envisaged molecular weight of the polymer and as a rule is in the range of 0.002 - 5 mol.%, based on the monomers.

To achieve higher polymerisation rates optionally small amounts of polar, aprotic solvent may be added. Suitable are, e.g., diethyl ether, diisopropyl ether, diethyleneglycol dimethyl ether, diethyleneglycol dibutyl ether, and tetrahydrofuran. The polar aprotic solvent as a rule is added to the hydrocarbon solvent in these process variants in a small amount of 0.5 - 5 vol.%, especially preferably 0.1 – 0.3 vol.%. Especially preferred is THF.

The invention will be further illustrated by the following Examples.

Example 1

Preparation of a copolymer from styrene and trans-stilbene with simultaneous introduction of the two monomers

A 250 ml round-bottom flask with an inert gas connection and septum was heated with a hot air blower and rendered inert in a nitrogen stream. Then 138.4 ml of ethyl benzene (120 g, 1.13 mol) and 19 g trans-stilbene (0.106 mol) were put in and heated to 60°C. Next, the solution was titrated out by the addition of sec-butyl lithium. After that 9.4 ml of a 0.32 molar solution of sec-butyl lithium in cyclohexane

(0.003 mol) were added as well as 12.1 ml (11 g, 0.105 mol) of styrene, in accordance with a previously calculated molecular weight of 10,000 g/mol, and polymerised for 6 hours at 70°C. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.
Yield: 13.59 g (45.3%), stilbene content (^{13}C-NMR) 9.2 mol.%, T_g (DSC) 110°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 6,637, M_W 8,032, M (peak maximum) 7,734.

Example 2
Preparation of a copolymer from trans-stilbene and styrene by the introduction of trans-stilbene and continuous dosing of styrene

A 1 l glass reactor with double jacket for heating and cooling and an anchor screw was rendered inert over the course of several hours with a refluxing solution of DPE/sec-butyl lithium in cyclohexane. After drawing off of the cleaning solution 403.6 ml of toluene (350 g, 3.8 mol) and 95.1 g trans-stilbene (0.528 mol) were put in and heated to 80°C. Next, the solution was titrated out by the addition of sec-butyl lithium. After that 3.0 ml of a 0.15 molar solution of sec-butyl lithium in cyclohexane (0.0015 mol) were added. Subsequently at 80°C 60.5 ml (54.9 g, 0.527 mol) of styrene, in accordance with a previously calculated molecular weight of 100,000 g/mol, were dosed continuously within 3 hours and then stirred again for 2 hours. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.

Yield: 63.15 g (42.1%), stilbene content (^{13}C-NMR) 28 mol.%, T_g (DSC) 129°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 47,900, M_W 120,900, M (peak maximum) 104,700.

Example 3

In a 250 ml glass flask with nitrogen connection were put 136.7 ml of ethyl benzene (118.6 g, 1.117 mol) and 19 g trans-stilbene (0.106 mol) and heated to 70°C. The solution was then titrated out by the addition of sec-butyl lithium. After that 1.8 ml of a 0.33 molar solution of sec-butyl lithium in cyclohexane (0.6 mmol) and 12.1 ml (11 g, 0.105 mol) of styrene, in accordance with a previously calculated molecular weight of 50,000 g/mol, were added and polymerised for 5 hours at 70°C. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.

Yield: 13 g (43.2%), stilbene content (^{13}C-NMR) 9.2 mol.%, T_g (DSC) 124°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 35,420, M_W 45,990.

Example 4

In a 1 l glass reactor were put under inert gas 270.5 ml of ethyl benzene (234.6 g, 2.21 mol) and 95.1 g of trans-stilbene (0.528 mol) and heated to 70°C. Next, the solution was added to by the addition of sec-butyl lithium in cyclohexane (15 mmol) and 60.5 ml (54.9 g, 0.527 mol) of styrene in 12 portions spaced 15 min apart, in accordance with a previously calculated molecular weight of 10,000 g/mol, and subsequently stirred again for 75 min at 70°C. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.

Yield: 92.85 g (61.9%), stilbene content (^{13}C-NMR) 20.8 mol.%, T_g (DSC) 139°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 5,425, M_W 6,435.

Example 5

In a 1 l glass reactor were put under inert gas 383.1 ml of toluene (333.9 g, 3.01 mol) and 95.1 g of trans-stilbene (0.528 mol) and heated to 50°C. Next the solution was titrated out by the addition of sec-butyl lithium. After that 10 ml of a 1.5 molar solution of sec-butyl lithium in cyclohexane (15 mmol) and 60.5 ml (54.9 g, 0.527 mol) of styrene were added in 12 portions spaced 15 min apart, in accordance with a previously calculated molecular weight of 10,000 g/mol, and subsequently stirred again for 75 min at 50°C. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.

Yield: 72.45 g (48.3%), stilbene content (^{13}C-NMR) 20.6 mol.%, T_g (DSC) 136°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 8,406, M_W 10,660.

Example 6

A 10 l steel kettle with a double jacket for heating and cooling and a MIG-stirrer was rendered inert overnight with activated solution (sec-butyl lithium in toluene with 1,1-diphenyl ethylene as indicator). After drawing off of the cleaning solution 6,916 ml of toluene (6,028 g, 65.42 mol) and 641 g of trans-stilbene (3.56 mol) were introduced and heated to 70°C. Next the solution was titrated out by the addition of sec-butyl lithium. After that 30.9 ml of a 0.566 molar solution of sec-butyl lithium in cyclohexane (0.018 mol) were added. Next at 70°C 1,222 ml (1,109 g, 10.65 mol) of styrene, in accordance with a previously calculated molecular weight of 100,000 g/mol, were dosed continuously within 5 hours and next stirred again for 1 hour. The living solution was titrated to colourlessness by the addition of ethanol and the polymer was subsequently precipitated by dropping the polymer

solution in ethanol. The white powder filtered off was washed several times with ethanol and dried *in vacuo* (1 mbar) for 12 hours at 100°C.
Yield: 1,352.8 g (77.3%), stilbene content (^{13}C-NMR) 13 mol.%, T_g (DSC) 130°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 75,560, M_W 171,000, M (peak maximum) 171,800, limiting viscosity (toluene, 30°C) [n] = 0.637 dl/g, residual monomers after GC: 1,179 ppm stilbene, 163 ppm toluene, styrene not detectable.

Example 7

The preparation took place as described in Example 6 (Repeat)
Yield: 1,258.2 g (71.9%), stilbene content (^{13}C-NMR) 12.5 mol.%, T_g (DSC) 131°C, molar mass (GPC, polystyrene calibration, g/mol): M_n 71,600, M_W 176,700, M (peak maximum) 176,600, limiting viscosity (toluene, 30°C) [n] = 0.666 dl/g, residual monomers after GC: 709 ppm stilbene, 237 ppm toluene, styrene not detectable.

TGA measurements on copolymers of styrene and stilbene

Product of Example	Comonomer in polymer wt.%	Tg °C	TGA (air) °C	TGA (N_2) °C
3	14.9	124	373	376
4	31.2	139	372	374
5	31	136	372	372

TGA: thermogravimetrics, TGA apparatus ex Netzsch (TG 209). Heating rate: 10 K/min, cleansing gas air or nitrogen, weight sample about 10 mg.

CLAIMS

1. Process for the preparation of copolymers based on 1,2-diphenyl ethene and styrene by polymerisation of the monomers
   a) 1 - 63 wt.% of 1,2-diphenyl ethene, wherein the aromatic nuclei can be substituted by up to 5 C_{1-12} alkyl groups, as component A,
   b) 37 - 99 wt.% of styrene, wherein the aromatic nucleus can be substituted by up to 5 C_{1-12} alkyl groups, as component B,
   c) 0 - 50 wt.% of further copolymerisable monomers as component C,
   with the overall amount of components A, B, and C being 100 wt.%, characterised in that component A and a polymerisation initiator are put in and components B and optionally C are continuously dosed to the polymerisation mixture.

2. Process according to claim 1, characterised in that as monomers
   a) 10 - 63 wt.% of trans-stilbene as component A and
   b) 37 - 90 wt.% of styrene as component B are used.

3. Process according to claim 1 or 2, characterised in that the polymerisation is carried out anionically.

4. Process according to any one of claims 1 - 3, characterised in that the polymerisation is carried out at a temperature in the range of 0 - 130°C and a pressure in the range of 1 - 10 bar.

5. Process according to any one of claims 1 - 4, characterised in that it is run in a hydrocarbon as solvent.

6. Process according to claim 5, characterised in that the hydrocarbon is selected from benzene, toluene, ethyl benzene, cyclohexane, methyl cyclohexane, xylene, and mixtures thereof.

7. Process according to any one of claims 1 - 6, characterised in that as polymerisation initiator sec-butyl lithium is used.

8. Copolymer obtainable by the process according to any one of claims 1 - 7.

9. Use of the copolymers according to claim 8 for the preparation of shaped bodies, fibres and foils.